

New Aspects of the High and Low Interstitial Concentration Desensitization of Silver Halide Emulsions

J. Siegel
Agfa-Gevaert AG, Leverkusen, Germany

1. Introduction

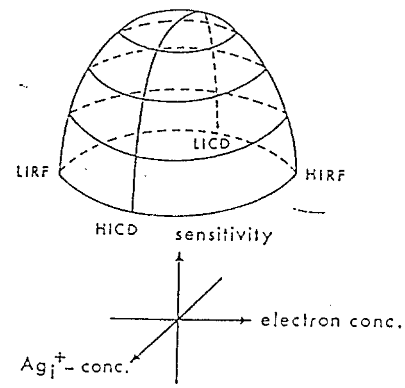
In the process of latent image formation silver clusters are formed by the interaction of light induced electrons and interstitial silver ions. The efficiency depends on many facts which were investigated and discussed very intensively.

Beside the composition of the AgX-grains the most important parameters are the following:

- the sensitivity centers, which are essentially created in the process of chemical ripening
- the electron concentration. For example it was found that the efficiency of latent image formation decreases if the electron concentration is too high or too low. This phenomenon is well known for a long time and described as High and Low Intensity Reciprocity Failure (HIRF and LIRF). The mechanism was discussed in different ways over a long time.
- the interstitial concentration. The subject of the authors investigations in the last years was the question in which way the Agi^+-concentration influences the latent image formation. It is known that the ionic conductivity of silver halide crystals depends essentially on their composition as well as on adsorbants. From Tani and van Biesen[1,2] it was shown, that antifoggants decrease the Agi^+-concentration and the sensitivity. Also adsorbed cyanine dyes influence not only the electron exchange with the silver halide. Furthermore there is an impact on the ionic properties[3-7]. Especially higher dye amounts increase the Agi^+-concentration.

This can lead - like it was shown - to a more disperse distribution of sublatent and latent image specks at the surface or in the grains volume and the result is desensitisation like in case of the stabilizers. This desensitization can be diminished by parameters which counteract against the dye induced increase of the interstitials. From Lapp, Harenburg and Siegel[8-10] it was shown that stabilizers like TAI are very effective to limit the desensitization at higher dye amounts. The same influence can be observed using crown or thio ether compounds.[11] Also a decrease of pH or pAg leads to a diminished ionic conductivity of the crystals and a smaller desensitization at higher dye amounts.[8]

Some years ago it was proposed to combine the dependence of the sensitivity from the electron - and Agi^+-concentration in a common model (Figure 1).



HICD - High Interstitial Concentration Densitization
LICD - Low Interstitial Concentration Densitization

In analogy to the HIRF and LIRF it was proposed to call the region, in which the sensitivity is decreased by a high Agi^+-concentration as HICD and the region, in which the Agi^+-amount is too low as LICD and the threedimensional body the sensitivity hyper surface.

In the following paper the real shape of the sensitivity hyper surfaces of cubic and octahedral AgBr grains are presented. The ionic conductivity of this grains was influenced by the adsorption of a sensitizing dye as well as by a crown ether and the stabilizer TAI. Furtheron the influence of iodide in the AgBr-grains will be discussed as well as the difference between the incorporation by conversion and precipitation.

2. Experimental

For the investigations are used kubic and octahedral AgBr grains. The ionic conductivity of this grains was influenced by the adsorption of 3,3´, 9-ethyl, 5,5´chloro-thiacarbocyanin as a sensitizing dye, the crown ether 4, 7, 13, 16-Tetraoxa-1,10-di-thiacyclooctadecan and Tetrazainden as a stabilizer.

The iodide was incorporated into the silver halide crystalls by conversion as well as douple jet precipitation.

The ionic properties were measured by the dielectric loss method. The frequency for which the dielectric loss has the maximum is proportional the interstitial concentration.

The High and Low intensity reciprocity failure was measured for irradiation into the silver halide as well as dye absorption between 10^{-4} and 10 s.

3. Results and Discussion

In Figure 2 there is given the sensitivity hyper surface for the octahedral grains and AgBr irradiation

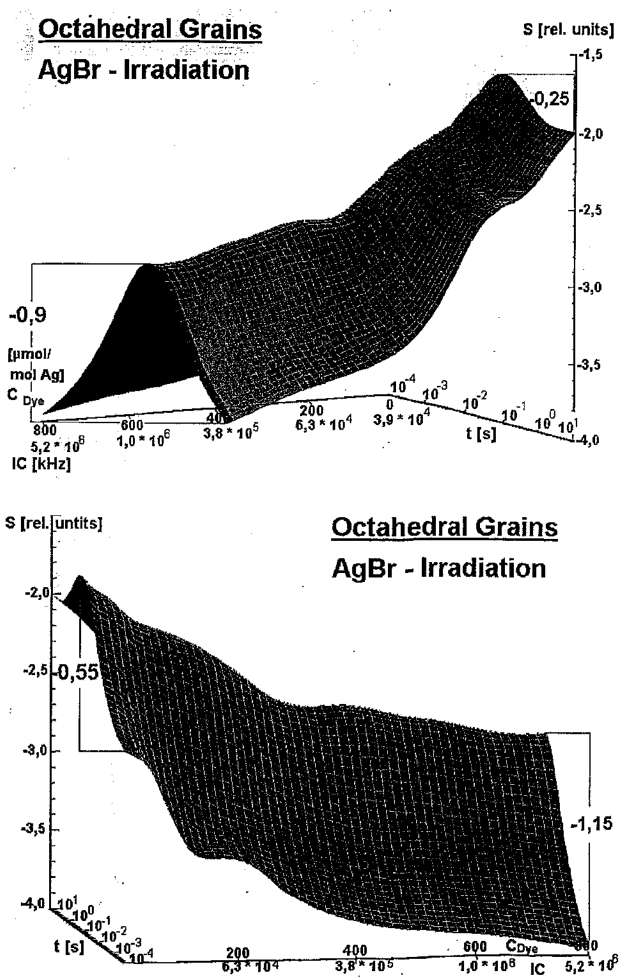


Figure 2.

This body describes the dependence of the intrinsic sensitivity from the electron concentration - given by the irradiation time - and the ionic conductivity. The conductivity was enhanced by increasing dye amounts. There is not a linear dependence between the dye concentration and Agi^+-concentration.

The following tendencies can be discussed. With an increase of Agi^+-concentration (respective dye amount) the desensitization will be enhanced. This is a well known phenomena. Furthermore the LIRF increases from 0,25 log. units in the case of unsensitized emulsion to 0,9 log. units at the highest ionic conductivity. Also the HIRF will be enhanced from 0,55 to 1,15 log. units.

For the interpretation of this behaviour there are two possibilities. The first one: The enlargement of the ionic conductivity leads to a higher dispersity of Ag-specks, to more small and nondevelopable Ag-clusters. Thats why the sensitivity will be decreased. In case of high electron concentration this dispersity will further be enhanced and the sensitivity decreases stronger. This agrees with the nucleation and growth model of Hamilton[12] which explain the HIRF by an increase of dispersity. On the other hand also the LIRF will be enhanced especially at the high Agi^+-concentration. This can be understand also with an increase of the dispersity of the latent image. At the high Agi^+-concentration there is a small probability that the formed Ag-atom grow to developable centres. Indeed this is in contrast to the nucleation and growth model which discusses the LIRF as an increase of the nucleation.

The second interpretation: Muenter and Hailstone[13] also investigated the HIRF/LIRF in the presence of a adsorbed dye for irradiation into the silver halide absorption. They used a dye with a low reduction potential which act especially as electron trap. This assumption should be applicable also for the dye which I've used. The dye is able to act as a trap for electrons from the conduction band. This means a loss of electrons for latent image formation and leads to an inefficient nucleation step especially in the case of a low intensity irradiation.

A different behaviour there was found in the case of the cubic grains. In Figure 3 there is shown the sensitivity hyper surface for irradiation into the AgBr-absorption.

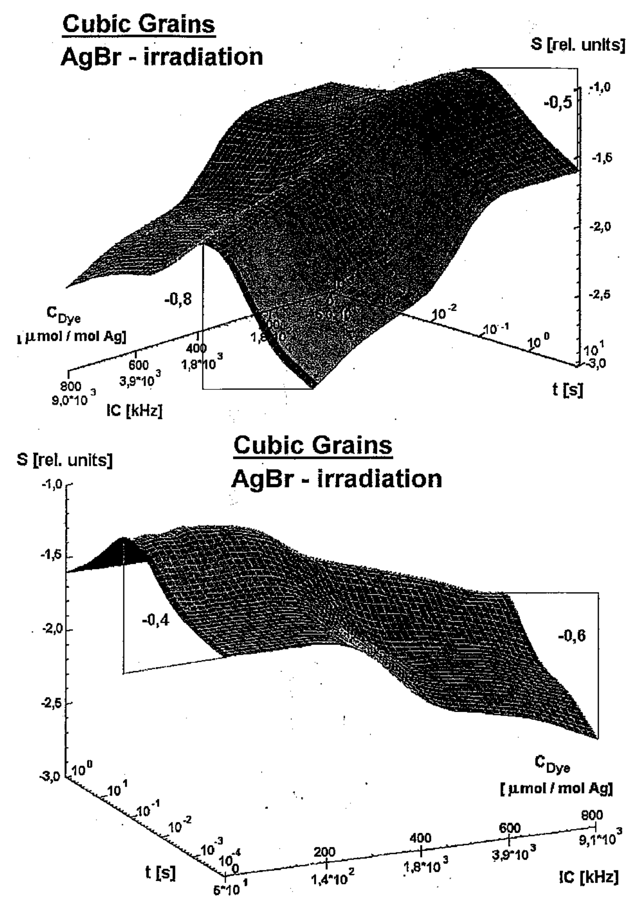


Figure 3.

Contrary to the octahedral grains the ionic conductivity is not as high and the increase at higher dye amounts not as strong. Desensitization occurs only for higher surface coverage and is not so enhanced like in case of the octahedral emulsion. Also the enhancement of the LIRF and HIRF is not as pronounced.

The differences between cubic and octahedral grains can be understand with the assumption that the Agi^+-concentration and their increase by adsorbed dye is the main effect for the desensitization and the change of HIRF and LIRF. The differences between cubic and octahedral grains are difficult to understand, if it will be assumed that the electron trapping by the dye is essential for desensitization and the increase of the reciprocity failure because the trapping efficiency should be the same in both cases. Until now it was shown only the part of HICD. Now there is presented additionally the region of LICD. At first for the AgBr irradiation of the cubic grains. The sensitivity hyper surface is given in the Figure 4.

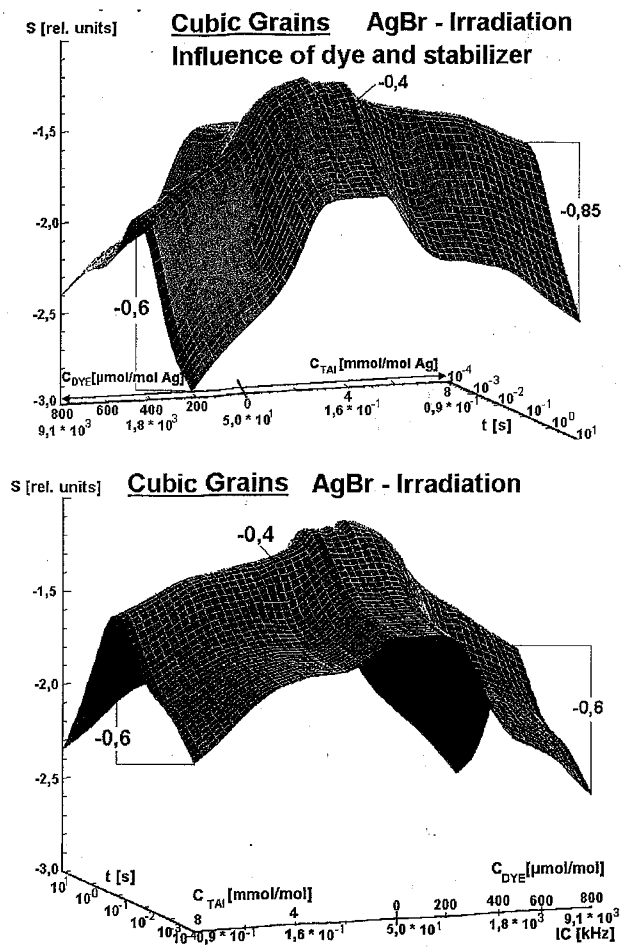


Figure 4.

The left part was discussed already with respect to the HICD. In the right part it´s shown the change of sensitivity if the ionic conductivity will be decreased (in this case by adsorption of TAI). The sensitivity will be diminished and the LIRF will be changed from 0,4 to 0,85 log. units and also the HIRF will be enhanced.

Obviously desensitization occurs not only if Agi^+-concentration is too high but also if the ionic conductivity is too low. And the effects are stronger especially if the electron concentration is not optimal.

This means that there exists an optimum of Agi^+ and e^--concentration concerning the efficiency of latent image formation. In case of the cubic grains, this optimum is obviously reached in case of the chemical ripened system. The behaviour is differently for the octahedral grains. The ionic conductivity is diminished also by the adsorption of TAI. But in this system the sensitivity is enhanced up to this region and the HIRF as well as the LIRF is lower (Figure 5).

Just at the lowest ionic conductivity desensitization can be found.

It seems to be that the difference in the behaviour between cubic and octahedral grains is the essential key for the understanding of the stabilizing effect of TAI which is discussed in the literature contrary. Sometimes it was reported that TAI shows a sensitizing effect (especially in case of AgBr,I-emulsions)[14] and sometimes that desensitization occurs - for instance in the case of AgCl-emulsions[15]. What is the reason for these differently effects?

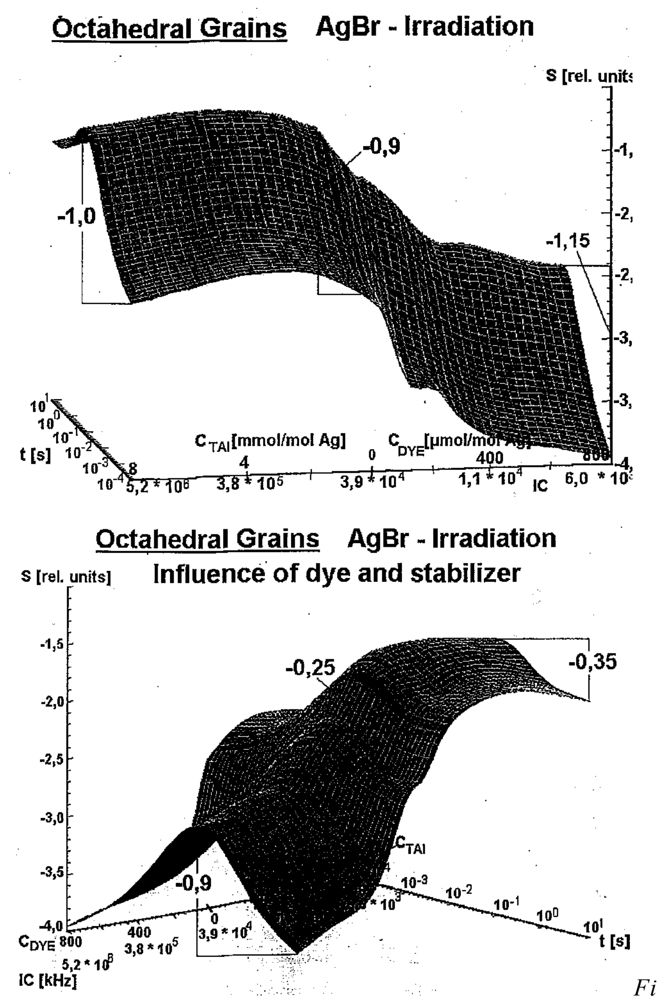


Figure 5.

The results show that the influence of the TAI depends on the fact, is the ionic conductivity of the emulsion without stabilizer optimal, too high or too low. If the Agi^+-concentration of the unstabilized emulsion is too high and thats why the efficiency of the latent image formation is not optimal, the adsorption of TAI leads to higher sensitivity. On the other hand if Agi^+-concentration without stabilizer is too low or optimal the adsorption of TAI leads to desensitization.

In the following there will be shown in principle that the same tendencies which were found at AgBr-irradiation also can be detected at dye irradiation of spectral sensitized emulsion. The same differences between the cubic and octahedral grains at irradiation into the silver halide absorption can be dedected in case of irradiation into the dye absorption. This means that the mechanism for the desensitization and the enhancement of the HIRF and the LIRF should be the same.

Furtheron it will be demonstrated, that the coadsorption of a crownether to the spectral sensitizer leads to a diminished Agi^+-concentration in the case of the unsensitized emulsion and there increase with higher dye amounts is not so strong. This leads to a decrease of the desensitization (like it was shown in [8]) as well as the HIRF and LIRF. The octahedral grains show in this case a behaviour more like the cubic emulsion.

Beside the adsorption of sensitizer and stabilizer the Ag_i^+-concentration is influenced essential by the silver halide composition. Iodide corporation during the precipitation leads to an increase of the ionic conductivity. It will be shown that for instance for the octahedral grains with 2 % iodide in the crystal especially the increase of ionic conductivity by the adsorption of the sensitizing is stronger than in the case the pure AgBr-emulsion. This leads to a more pronounced desensitization and an increase of HIRF and LIRF in the case of higher dye amounts. These results are in good agreement with the assumption that the enhancement of Ag_i^+-concentration leads to a higher dispersity of the latent image specks and desensitization especially in case of high and low electron concentration.

On the other hand the incorporation of iodide leads not in every case to an influence of the HIRF and LIRF. In case of iodide conversion at the surface of AgBr octahedrals the ionic conductivity will be also enhanced. But in contrast to the iodide corporation during precipitation the increased Ag_i^+-concentration leads not to a change of the LIRF as well as the HIRF. It seems that the reason for this behaviour is the ionic and electronic relaxation in the phase boundary between AgBr and AgI. This leads to a high efficiency of latent image formation and the dispersity of the developable Ag-clusters will not be influenced by an increase of interstitial concentration.

Acknowledgement

The author thanks D. Vandenbroucke and R. De Keyzer from Agfa-Gevaert Mortsel for many helpful discussions and the most measurements of the reciprocity behaviour of the investigated emulsions.

References

1. J. van Biesen, *J. Appl. Phys.*, **41** (1970) 1910
2. T. Tani, *J. Phot. Sci.*, **28** (1980) 28
3. T. Tani, Proceedings ICPS'86 Köln, p. 335
4. T. Tani, *Phot. Sci. Eng.* **18** (1974) 629
5. H. G. Rollar, K. Hoffmann, Proceedings ICPS'86 Köln, p. 370
6. J. Siegel et. al., *J. Phot. Sci.*, **38** (1990) 47
7. J. Siegel et. al., *J. Inf. Rec. Mat.*, **18** (1990) 197
8. J. Siegel, O. Lapp, *Bulg. Chem. Comm.*, **26** (1993) 339
9. J. Siegel, D. Vandenbroucke, Proceedings ICPS'94 Rochester, p. 132
10. J. Harenburg et. al., Proceedings ICPS'94 Rochester, p. 134
11. Y. Steidel et. al., Proceedings IS&T-Meeting 1996, Minneapolis
12. J. F. Hamilton, *Phot. Sci. Eng.*, **18** (1974) 371
13. A. A. Muenter, R. K. Hailstone, The East West Meeting II; Hawaii 1988, F 11
14. E. J. Birr, Stabilization of photographic silver halide emulsions, Focal Press London/New York (1974), p. 140 - 212
15. P. Faelens, *J. Phot. Sci.*, **23** (1985) 86.